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Investigation of the effect of interaction conditions on the development of the internal network structure of crumb rubber–modified asphalt (CRMA) was carried out. Enhancements in the CRMA physical properties, such as stiffness, expressed in the complex modulus (G^*), and elasticity, expressed in the phase angle (δ), as a result of the development of three-dimensional (3-D) entangled network structure were achieved. These results came from controlling the interaction conditions of CRMA synthesis to regulate the crumb rubber–modified (CRM) components that were responsible for the formation of the 3-D entangled network structure. Dissolution tests and thermogravimetric analysis (TGA) were performed on the extracted CRM particles after interaction with asphalt. A Fourier transform infrared (FTIR) spectroscopy investigation was performed on the liquid phase asphalt after separation of CRM. FTIR was used to investigate the state of the released CRM components, previously calculated by TGA, which were responsible for the formation of the 3-D network structure. Use of rheological, TGA, and FTIR tests confirmed that the enhancement of the CRMA's G^* and δ was dependent on the dissolution or release of CRM components under specific interaction conditions that led to the existence of a 3-D network structure within the liquid phase of the CRMA. The development of the 3-D entangled network structure in CRMA was found to be attributable to the release of most of the CRM natural and synthetic rubber components under specific interaction conditions. Enhancements in the CRMA G^* and δ provided improved rutting resistance and alleviated permanent deformation problems.

Asphalt is made up of continuous three-dimensional (3-D) associations of polar molecules dispersed in a fluid of nonpolar or relatively low-polarity molecules (*1*). The polar functions in asphalt form associations of various strengths (*1*). The typical viscoelastic properties for neat asphalts are formalized as a result of the continuous formation and breakage of these associations under the effects of external factors such as shear stresses and temperature variations (*1*).

Attia and Abdelrahman (*2*) and Abdelrahman (*3*) highlighted the effect of interaction between asphalt, crumb rubber–modified (CRM), and virgin polymer (VP) on the physical properties of the modified asphalt. They stated that more elasticity is added to asphalt as a result of depolymerization (of rubber), which appears to have the largest effect on modifying the phase angle. Based on their work, the development of a network in the binder structure can be anticipated from the values of complex modulus (G^*) and phase angle (δ) that are dependent on the material exchange between asphalt, CRM, and VP. Simultaneously, Saylak et al. discussed the existence of a direct relationship between the values of the elastic component and the degree of cross-linking of the material that gives the material its elastic characteristics (*4*). This direct relationship indicates that δ can be utilized to monitor the binder polymeric structure. In another work, Bahia and Davies discussed existence of some type of interaction phenomenon that changes the nature of the liquid phase while increasing the effective volume of the rubber particles (*5*).

The utilization of a compatible polymer for mixing with asphalt results in the absorption of the low molecular weight oil fraction of the base asphalt by polymer strands (*1, 6*). 3-D entangled networks are formalized when these swollen strands can connect together at domains or nodes. These networks significantly affect the mechanical properties of polymer modified asphalts (PMA) and ultimately the asphalt concrete mixes (*1*). When the networks are destroyed or disturbed by shear flow, they can re-form with time and impart the ability of self-healing to the PMA (*1*).

The interaction between CRM and asphalt results in modification of the asphalt by the swelling of CRM particles through absorbing the light aromatics of asphalt, CRM components released into the liquid phase of asphalt, or both mechanisms simultaneously (*7, 8*). It has been suggested that severe interaction conditions of combined high interaction temperature and mixing speed results in having the devulcanization and depolymerization process as governing mechanisms leading to the release of the CRM polymeric chains into the asphalt liquid phase (*8, 9*). In a limited study, Ghavibazoo and Abdelrahman investigated the CRM main components released into the asphalt matrix during its dissolution in asphalt (*10*).

The effect of the control of the interaction parameters between CRM and asphalt on the development of a 3-D entangled network structure in the liquid phase of the crumb rubber–modified asphalt (CRMA), leading to superior rutting and permanent deformation resistance, has been previously investigated (*11*). However, up to this point no work has been carried out to investigate the relationship between the CRM dissolved components and the development of 3-D entangled network structure in CRMA to produce CRMA with superior enhanced physical properties.

The aim of this work was to investigate the effect of the dissolved amounts of CRM and released components on the enhancement of the physical properties of CRMA as a result of the participation of such released CRM components in the development of a 3-D entangled network structure in CRMA.

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MATERIALS AND EXPERIMENTAL PROCEDURES

Processing

Raw Materials

Two asphalt binders were investigated in combination with one type of crumb rubber. The asphalts were PG 52-34 (HU-52) and PG 64-22 (HU-64), based on the Superpave® grading system. The CRM was cryogenically processed from a mixed source of scrap tires. The CRM particle size was smaller than mesh No. 30 and larger than mesh No. 40, according to the U.S. standard system.

Asphalt–CRM Interactions

The interactions were conducted in 1-gal cans and a heating mantle connected to a bench-type controller with a long temperature probe (12 in.) used to heat the material. A high shear mixer was used to mix the binder and CRM. The amount of CRM was controlled to be 10% of the weight of the asphalt in all interactions. Interactions were conducted for 480 min under a combination of three temperatures (160°C, 190°C, and 220°C) and three mixing speeds (10, 30, and 50 Hz). Samples were taken at 15, 60, 120, 240, and 480 min interaction times and kept at −12°C to avoid any unwanted reactions. All interactions in this research were carried out under a controlled atmosphere of nitrogen gas to prevent any oxidation. A specific coding for the samples was adopted, starting with the asphalt type, HU-52 or HU-64, followed by the interaction speed, interaction temperature, and interaction time, if required.

Characterization

Dynamic Mechanical Analysis

A dynamic shear rheometer was used for dynamic mechanical analysis of the modified asphalt. All tests were conducted at 70°C and 10 rad/s. Samples were tested on 25 mm parallel plates with a 2 mm gap. Utilization of a 2 mm gap to test CRMA by a dynamic shear rheometer has been carried out by various researchers (*12*).

Dissolution Test

To investigate the effect of CRM dissolution on the CRMA properties, dissolution tests were conducted on all CRMA samples through extraction of CRM from CRMA samples with a mesh No. 200. In this method, 5±2 g of CRMA was diluted in toluene and drained through a mesh No. 200. The retained particles were washed with extra toluene, until the filtrate became colorless, and dried in the oven at 60°C to ensure removal of all solvent residues. Dissolved CRM amounts represent the difference between the expected weight of the CRM and the actual weight of the CRM after extraction from a CRMA sample of known weight.

Thermogravimetric Analysis

For the thermogravimetric analysis (TGA) testing, ASTM E-1131 standard was followed with minor modifications to conduct composition analysis on the CRM before and after interaction with the asphalt. The received and extracted CRM samples were heated to 600°C by utilizing a heating rate of 20°C/min. To distinguish between the different components in a multicomponent sample like CRM, the sample is heated to high temperatures while monitoring the loss of mass caused by decomposition as a function of temperature and simultaneously graphing in a thermograph (*13, 14*). The thermogravimetric method of analysis has been utilized by several researchers to investigate the composition of multicomponent polymeric materials including CRM (*10, 13–15*).

To investigate the changes in composition of CRM samples during interaction with asphalt, the decomposition temperature range of each component in the CRM samples was obtained from their mass loss rate in the related derivative of the thermograph and temperatures reported in other studies (*10, 16, 17*). Based on the decomposition temperature ranges for each component in the CRM sample, the related TGA curve was divided into four regions (*10*). The first region (25°C to 300°C) was related to the oily components in the CRM, the second region (300°C to the minimum (mid) point between the two peaks in the derivative of the thermograph curve) corresponded to the natural rubber portion of the CRM, and the third region (second region to 500°C) corresponded to the synthetic rubber portion of the CRM. Finally, the residue at 500°C corresponded to filler components, like carbon black, in the CRM (*10*). For brevity, only the derivative of the thermograph curve for the HU-52–50 Hz–160°C–60 min extracted CRM sample is illustrated in Figure 1, although similar graphs were obtained for all the samples that were investigated.

Fourier Transform Infrared Spectroscopy

A mesh No. 200 was used to separate asphalt samples from CRM. The material passing through the sieve was considered the CRMA liquid phase. The CRMA liquid phase was then diluted in toluene with a concentration of 50 mg per each mL of toluene. Samples were laid on the KBr disks and left for a period of 15 min to ensure that the solvent had completely evaporated. Transmission spectroscopy was carried out with a two-face polished KBr disk. Thirty-two scans were employed. The resolution was 4 with wave numbers ranging from 1,600 to 600 cm^{-1}.

RESULTS AND DISCUSSION

Rheological Analysis of the CRMA

Figures 2 and 3 illustrate the development of the rheological parameters, $G^*(I)$ and $\delta(II)$, for the two asphalt types investigated (HU-52 and HU-64) interacted at: 50 Hz and 160°C (Figure 2, *a* and *d*), 10 Hz and 190°C (Figure 2, *b* and *e*), 30 Hz and 190°C (Figure 2, *c* and *f*), 50 Hz and 190°C (Figure 3, *a* and *d*), 10 Hz and 220°C (Figure 3, *b* and *e*), and 50 Hz and 220°C (Figure 3, *c* and *f*). As shown in Figure 2, *a*, *b*, and *c*, a continuous increase in the G^* values can be seen for the two CRMA types investigated, with the HU-64 CRMA samples having higher G^* values over the other HU-52 samples.

Under the combination of low interaction temperature (160°C) and high mixing speed (50 Hz), the only governing parameter for the enhancement in G^* is the particle effect of swollen CRM in the asphalt as a result of the absorption of light molecular aromatics (*7*), as will be proven later in the thermal analysis section. By contrast, the higher values of G^* for the HU-64 CRMA samples over the HU-52 samples can be attributed to the fact that the HU-64 asphalt is a stiffer binder and thus it is expected that it would give higher G^* values.

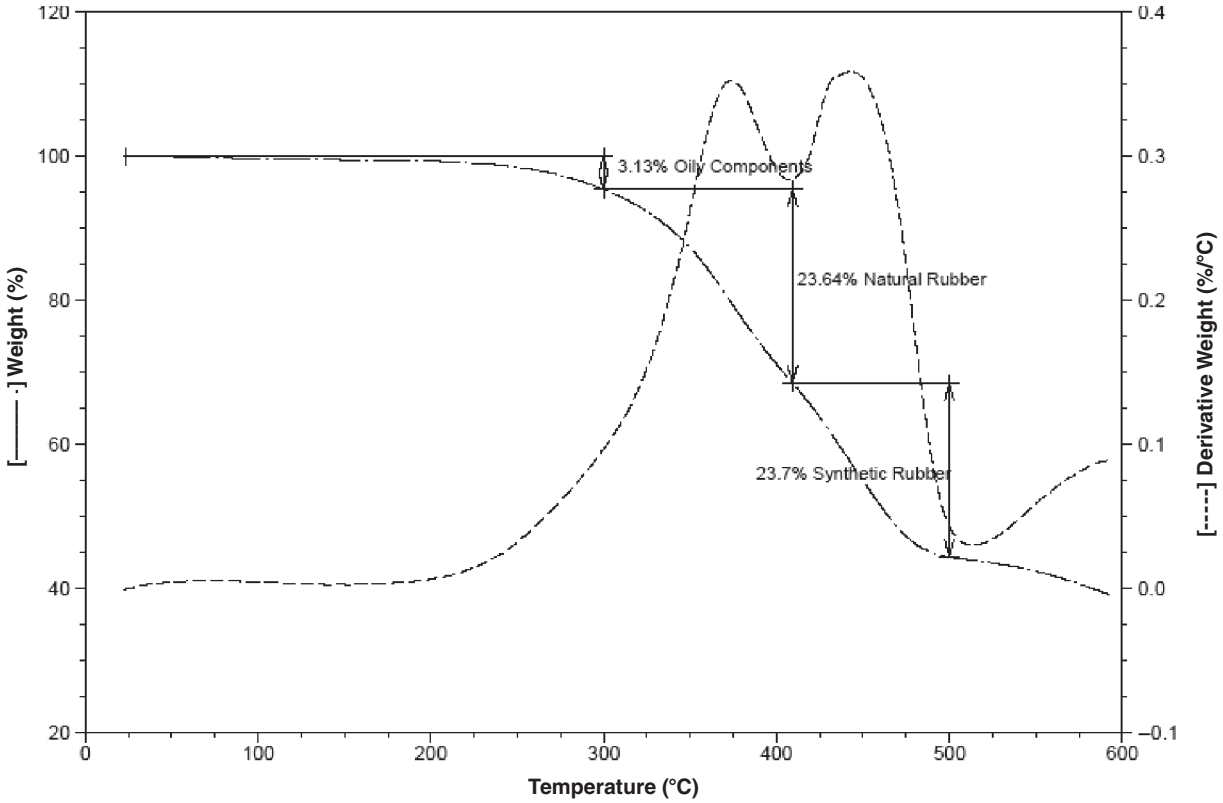

FIGURE 1 TGA curve analysis for HU-52-50 Hz-160°C-60 min extracted CRM sample.

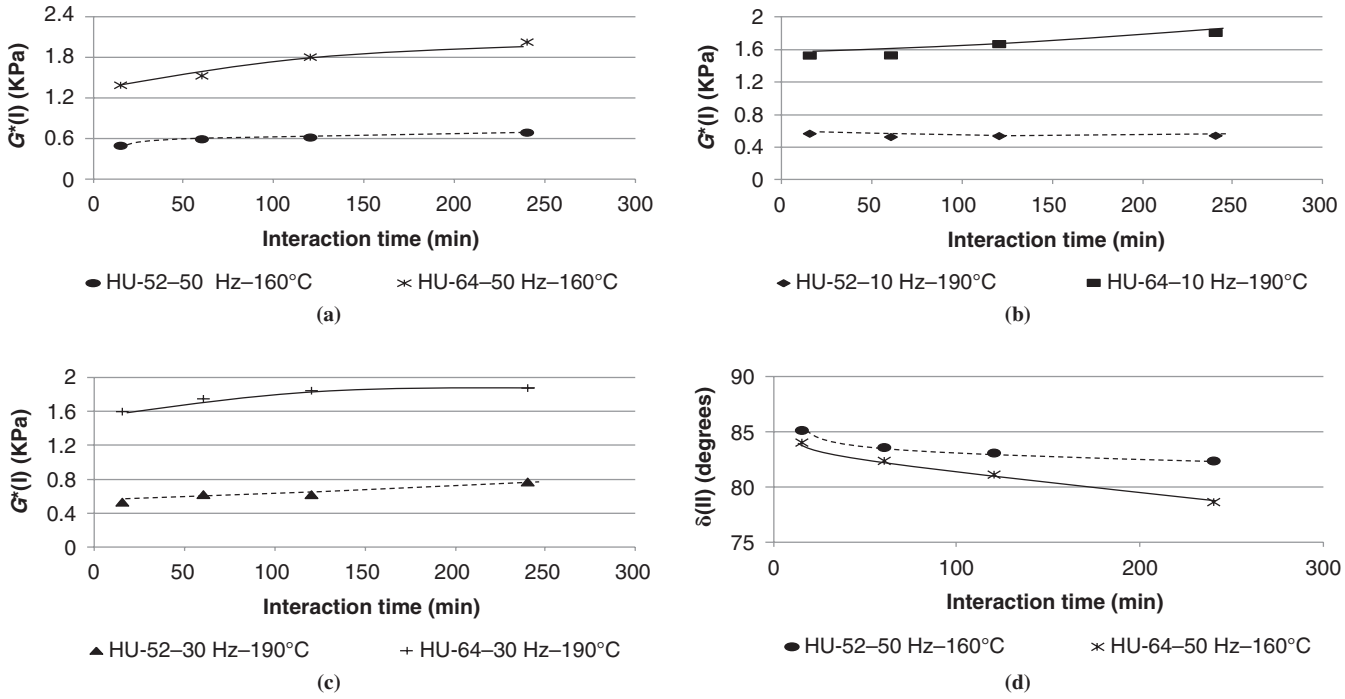

FIGURE 2 Development of rheological parameters of CRMA: (*a*) G^*, 50 Hz, and 160°C; (*b*) G^*, 10 Hz, and 190°C; (*c*) G^*, 30 Hz, and 190°C; and (*d*) δ, 50 Hz, and 160°C.

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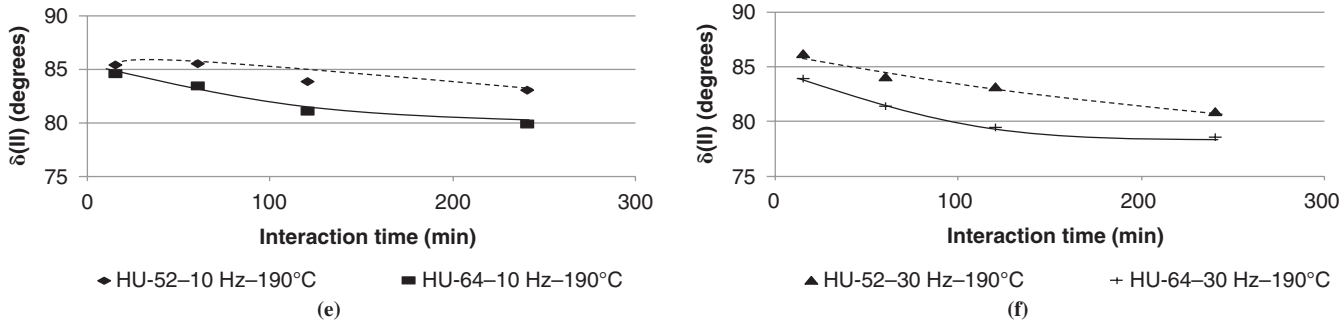


FIGURE 2 *(continued)* Development of rheological parameters of CRMA: (*e*) δ, 10 Hz, and 190°C and (*f*) δ, *G**, 30 Hz, and 190°C.

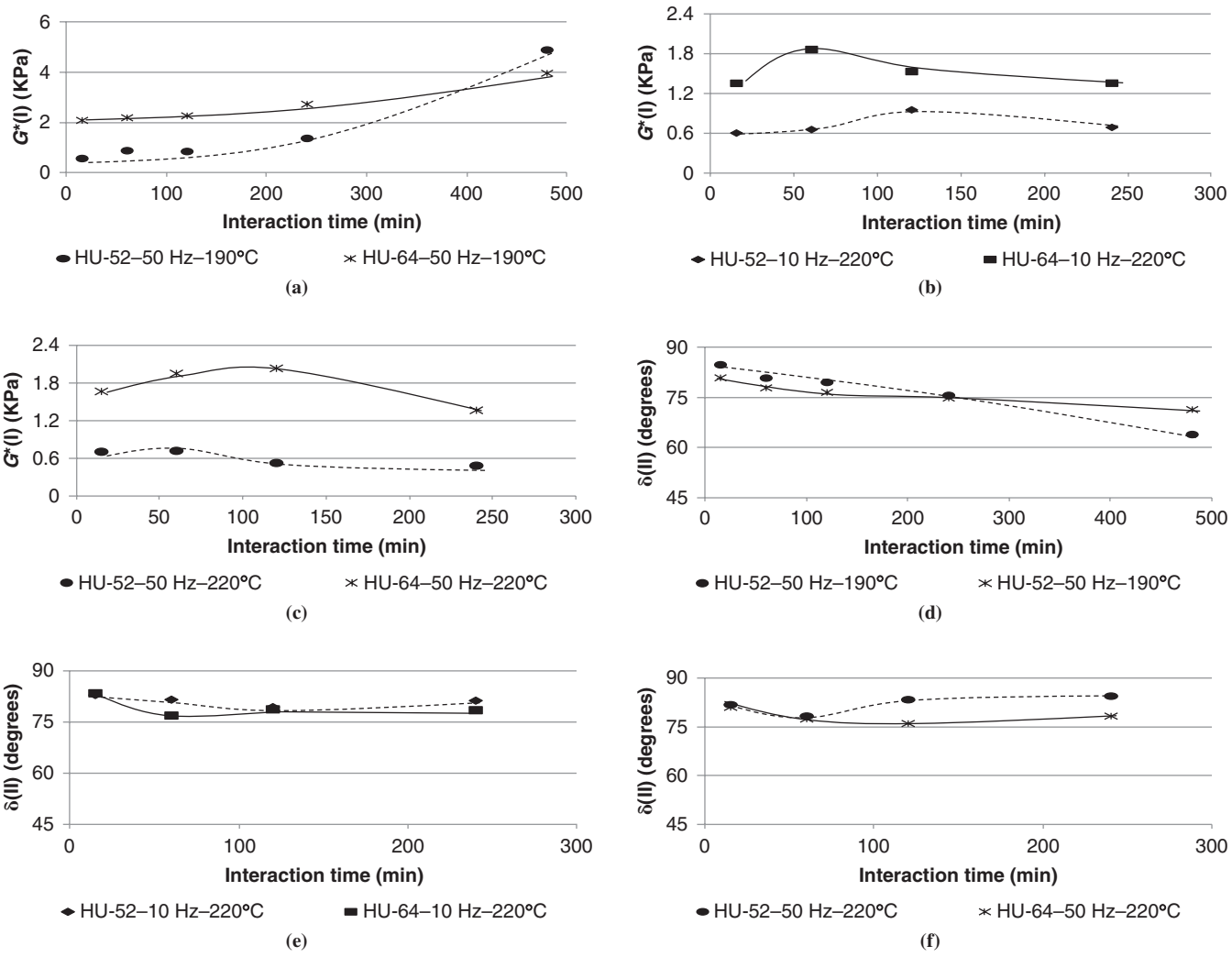


FIGURE 3 Development of rheological parameters of CRMA: (*a*) *G**, 50 Hz, and 190°C; (*b*) *G**, 10 Hz, and 220°C; (*c*) *G**, 50 Hz, and 220°C; (*d*) δ, 50 Hz, and 190°C; (*e*) δ, 10 Hz, and 220°C; and (*f*) δ, *G**, 50 Hz, and 220°C.

Figure 2*d* shows the same trend for δ °C. A reduction in the value of δ can be seen for both CRMA types investigated, with the HU-64 CRMA samples showing better values over the HU-52 samples. However, for both CRMA types investigated, the enhancements in the *G** and δ values are minor. This was because at such a low interaction temperature (160°C) and even with the utilization of a higher mixing speed (50 Hz), the release of CRM components was not sufficient to lead to the formation of a 3-D network structure in the liquid phase of the CRMA that would dramatically enhance its *G** and δ values; a similar observation was made in previous work with a different type of asphalt (*11*). This insufficiency can be explained as a result of the restriction of CRM particle activity on absorption of light molecular aromatics (*7*). Sufficient release of CRM components under specific interaction conditions would have led to the formation of a 3-D network structure in the liquid phase of the CRMA, providing enhancement in the *G** and δ values, as will be proven in the thermal analysis section.

Figure 2*b* shows superior values of *G** for the HU-64 CRMA samples over the HU-52 CRMA samples during the interaction time. However, the combination of the moderate temperature of 190°C and low speed of 10 Hz with the associated minor release of CRM components into the liquid phase of CRMA was not sufficient to initiate and sustain the formation of the 3-D network structure in the liquid phase of CRMA. A similar behavior can be seen in Figure 2*e* for the δ property progression with the interaction time, where the δ values continue their enhancement with the increase of interaction time with the HU-64 CRMA samples showing better enhancement over the HU-52 CRMA samples.

Figure 2*c* shows a weak plateau behavior for both asphalt types investigated, with the HU-64 samples of higher values than the HU-52 samples. Figure 2*f* illustrates the same trend for δ enhancement in which the HU-64 samples exhibit lower values than the HU-52, when measured for the same interaction time. The enhancement in the *G** and δ values for these interaction conditions can be explained in terms of the swelling and minor depolymerization or devulcanization of the CRM (*7*). The minor release of CRM components was not sufficient to initiate or sustain the development of a 3-D network structure that would have produced major enhancement in the rheological parameters investigated, *G** and δ, as will be proven in the thermal analysis section. However, with the increase of interaction speed, temperature, and time, property enhancement, in terms of increased *G** and reduced δ, is achieved because of the increase in the rate of dissolution of the CRM and thus the addition of CRM components into the liquid phase of asphalt.

As shown in Figure 3*a,* a major enhancement in the value of *G** can be seen for the CRMA when both the HU-52 and HU-64 asphalts are used, having the CRMA made with HU-52 of higher values than the HU-64 CRMA after 480 min of interaction time. The same trend can be seen for the δ values shown in Figure 3*d.* Similar observations were recorded in previous work that used another asphalt type (PG 58-28) (*11*). It was proven that such behavior was attributable to the formation of a 3-D network structure in the liquid phase of the CRMA (*11*). However, in that study, it was speculated that the reason for the formation of the 3-D network structure was because of the release of CRM components into the liquid phase of the CRMA. Under the interaction parameters (interaction temperature 190°C, mixing speed 50 Hz, and interaction time 480 min), it was possible to maintain and preserve the CRM components and associate them with the components of the liquid phase of asphalt (*11*). In the study reported here, through the utilization of the TGA and Fourier transform infrared (FTIR) techniques, the previous speculation was proved for the analysis of the CRM extracted as well as the liquid phase from the two asphalt types.

As shown in Figure 3*b,* for both asphalt types investigated, the values of *G** suffer deterioration alongside the interaction time, after a brief increase within 60 min of the interaction time for HU-64 and 120 min for HU-52. The same observation can be drawn for the δ values, as illustrated in Figure 3*e.* Unlike what occurs for moderate (190°C) interaction temperature with the utilization of low (10 Hz) interaction speed, the utilization of a high interaction temperature (220°C) leads to destruction of released CRM components by excessive depolymerization and devulcanization, as can be seen from the deteriorated *G** and δ values (*8, 9*).

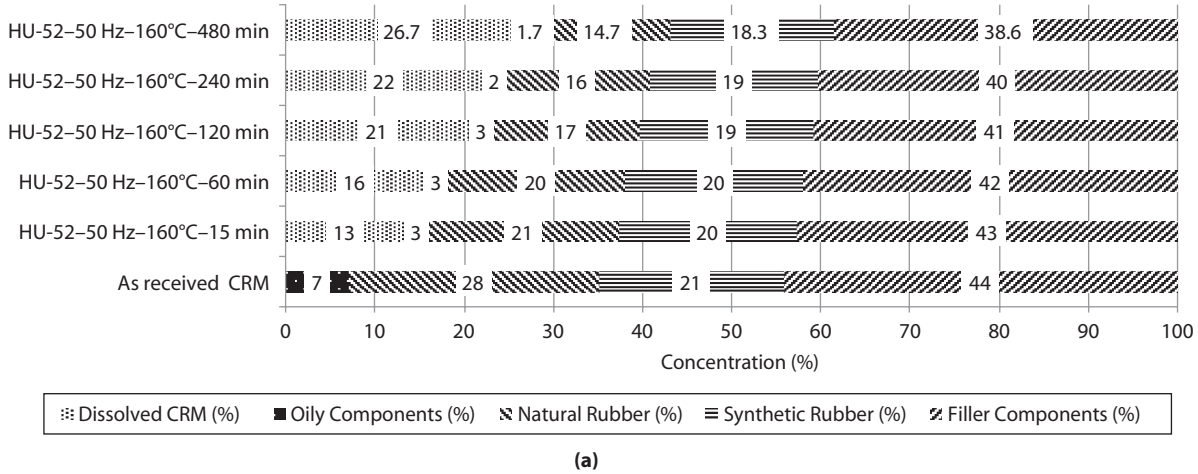
As shown in Figure 3*c,* property deterioration is prevalent after 120 min of interaction time for both asphalt types investigated (HU-64 and HU-52). A similar trend of property deterioration can be seen for the δ behavior illustrated in Figure 3*f,* where the δ values show a consistent increase after 60 min of interaction time for the HU-52 samples and after 120 min of interaction time for the HU-64 samples. The main reason behind the property deterioration is the excessive depolymerization and devulcanization effects that were increasingly manifested at the combination of high interaction temperature (220°C) and mixing speed (50 Hz) (*8, 9*). The combination led to the destruction and annihilation effects of the CRM components that were released at the CRMA liquid phase.

Thermal Analysis of Extracted CRM

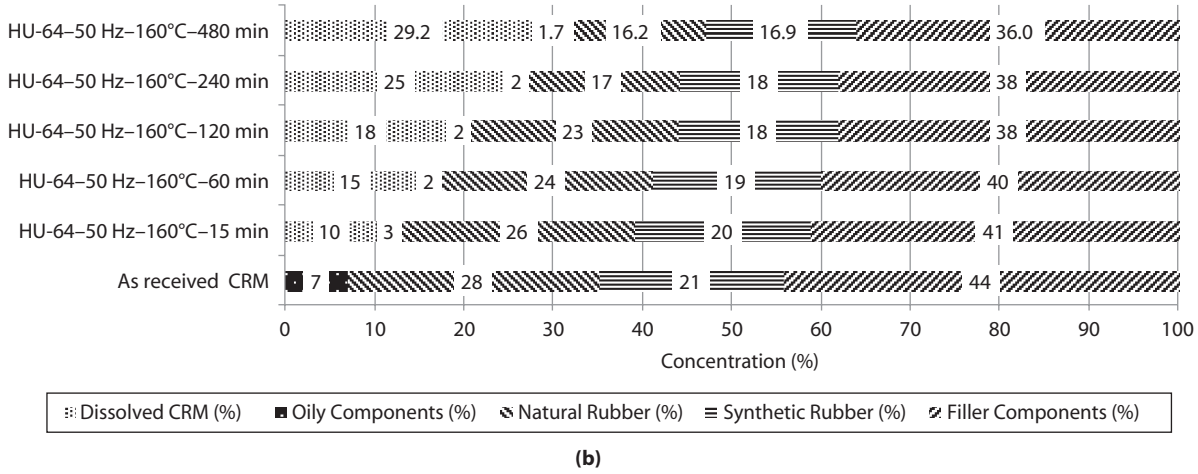
Figure 4, *a* and *b,* illustrates the change in compositional analysis of extracted CRM for the samples interacted at a temperature of 160°C and mixing speed of 50 Hz for both asphalts. As shown in Figure 4*a* for the extracted CRM from HU-52, utilization of an interaction time of 15 min resulted in a 13% partial dissolution in CRM with the major components released expressed in terms of oily components and natural rubber. The dissolution of CRM increases to 16%, 21%, 22%, and 26.7% for the 60, 120, 240, and 480 min interaction times, respectively. The increase in dissolution of CRM is associated with a major release of most of the oily components, as well as natural rubber, whereas minor release of the synthetic rubber and the filler components can be seen, even after 480 min of interaction time.

The same trend can be seen for the compositional analysis of extracted CRM from HU-64 CRMA, which is illustrated in Figure 4*b.* Almost the same dissolved amounts can be found for the CRM extracted from the HU-52 and HU-64 CRMA samples. Relating the released CRM components to the rheological behavior of CRMA illustrated in Figure 2, *a* and *d,* implies that the weak enhancement in the CRMA rheological properties, *G** and δ, can be explained in terms of the minor release of CRM components that were not sufficient to initiate or sustain a 3-D entangled network structure. Under such low interaction temperature (160°C) and even with the utilization of a high mixing speed (50 Hz), the main CRM activity controlling the CRMA performance was mainly the swelling of CRM (*7*).

Figure 5 shows the variation in compositional analysis of extracted CRM with the increase of interaction time for the samples: HU-52–10 Hz–190°C (Figure 5*a*), HU-64–10 Hz–190°C (Figure 5*b*), HU-52–30 Hz–190°C (Figure 5*c*), and HU-64–30 Hz–190°C (Figure 5*d*). Figure 5 illustrates an increase in the CRM dissolution rate for CRM samples extracted from both asphalt types investigated as compared with the dissolution rates for the CRM extracted under interaction conditions of 160°C and 50 Hz, as illustrated in Figure 4, *a* and *b.* The increase indicates that the effect of the interaction temperature



(a)



(b)

FIGURE 4 Component concentration in extracted CRM samples in comparison with original CRM: (*a*) HU-52–50 Hz–160°C and (*b*) HU-64–50 Hz–160°C.

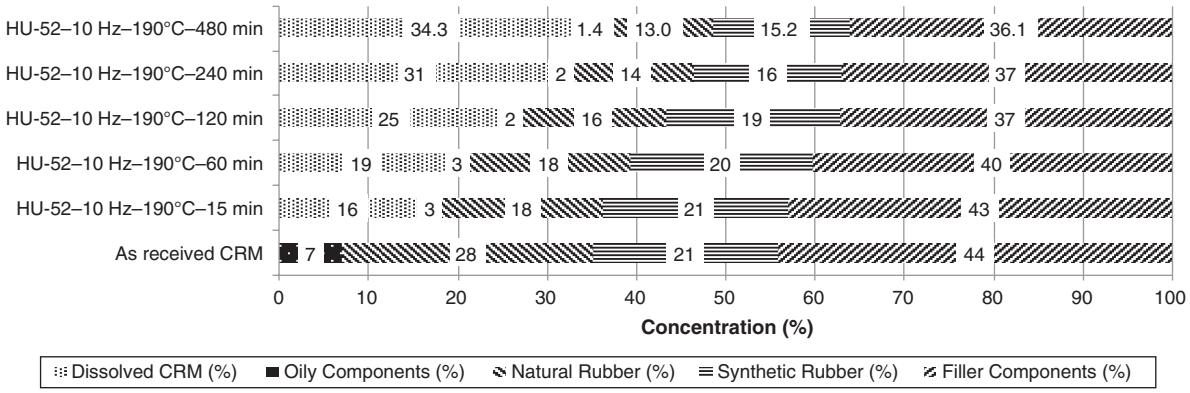
is prevalent over the effect of the interaction speed in controlling the dissolution rate of CRM and thus property enhancement of CRMA.

Figure 5, *a* and *b,* illustrates the minor release of the synthetic rubber and filler components from the CRM into the liquid phase of asphalt alongside the interaction time. By contrast, release of the oily components and the natural rubber is abundant with the increase in interaction time. The minor release of CRM components had a similar effect as that of the samples interacted at 160°C and 50 Hz. The CRM-released components were insufficient to initiate or sustain a 3-D entangled network structure that would have enhanced the G^* and δ significantly. The rheological results are illustrated in Figure 2, *b* and *e,* where minor property enhancements can be seen for both G^* and δ, with the main cause being the CRM particle swelling in the presence of minor CRM-released components. Figure 5*c* shows that, for the extracted CRM from HU-52 CRMA interacted at 30 Hz and 190°C, the same trend that was observed earlier for the samples interacted at 50 Hz and 160°C manifested in the release of most of the oily components, as well as natural rubber. There was a minor release of both the synthetic rubber and the filler components, even after 480 min of interaction time.

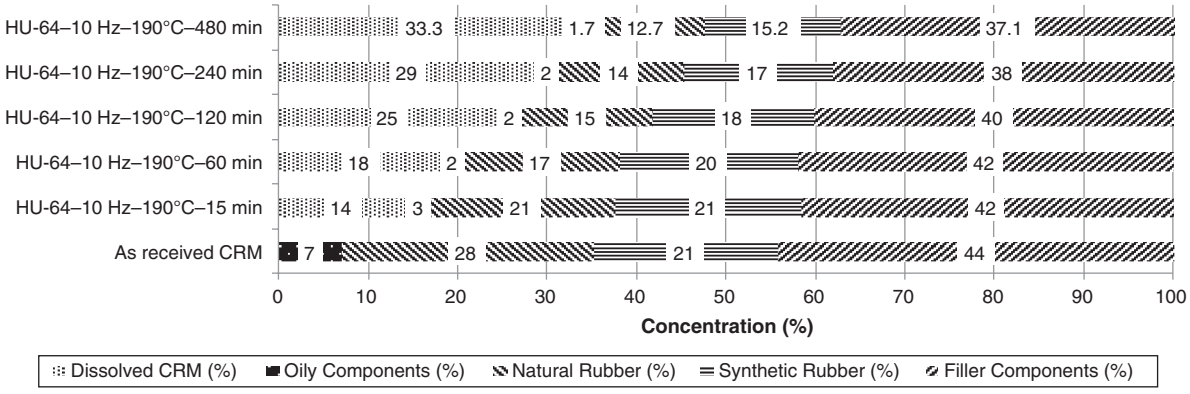
There was a similar trend for the compositional analysis of extracted CRM from HU-64 CRMA, as illustrated in Figure 5*d.* After 480 min of interaction time, the oily components reached 1.2% and the natural rubber reached 10.8% from their original values of 7% and 28%, respectively. The synthetic rubber decreased from 21% to 14.3% and the filler components reached 36.2% from an original value of 44%. Relating these results to the G^* and δ values illustrated in Figure 2, *c* and *f,* shows that the lack of abundance of CRM-released components at such interaction conditions resulted in minimized property enhancements.

Figure 6 illustrates the change in compositional analysis of extracted CRM with an increase in interaction time for the samples interacted at 190°C and 50 Hz for HU-52 CRMA (Figure 6*a*) and HU-64 CRMA (Figure 6*b*). A different behavior for the dissolution as well as the discharge of CRM components can be seen at this combination of moderate interaction speed (190°C) and high mixing speed (50 Hz).

As shown in Figure 6*a,* utilization of an interaction time of 15 min resulted in a 25% partial dissolution in CRM with the major components released expressed in terms of oily components and natural rubber. However, extending the interaction time to 480 min resulted in a major release of CRM components that manifested in increased CRM dissolution to 30%, 62%, 78%, and 83% for interaction times of 60, 120, 240, and 480 min, respectively. The increase in dissolution of CRM is associated with a major release of most of the CRM components after 480 min of interaction time, where the oily components reached 0.5%, the natural rubber reached 4%, the synthetic rubber reached 3%, and the filler components reached 10%, from original values of 7%, 28%, 21%, and 44%, respectively.



(a)



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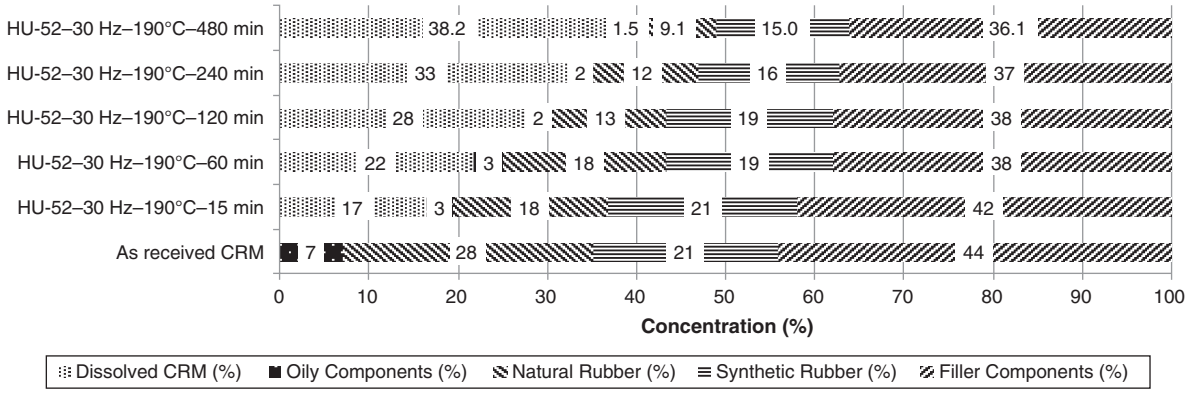
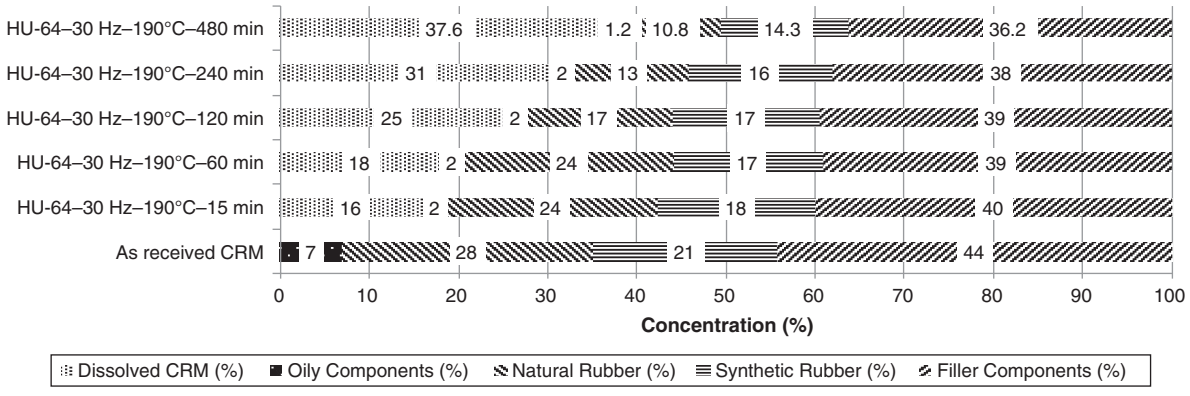
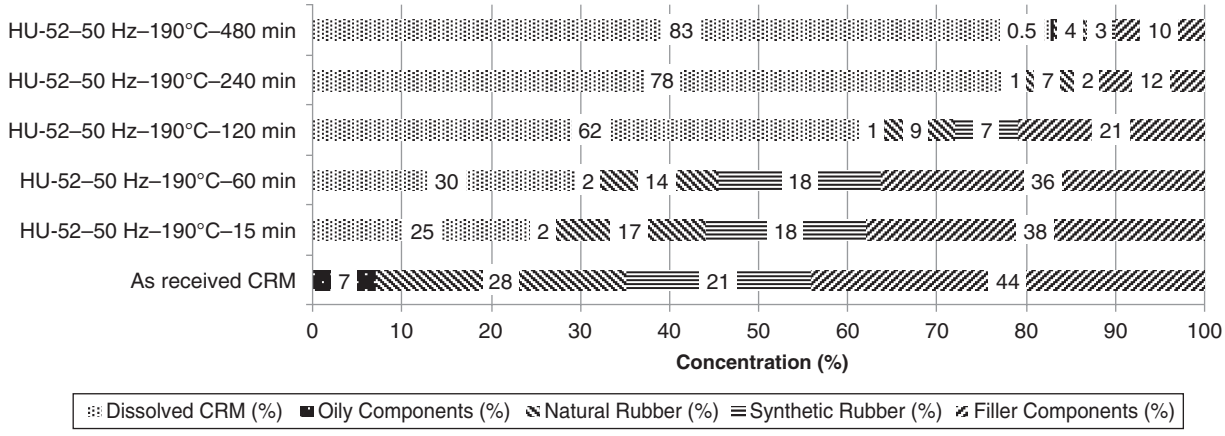


(c)

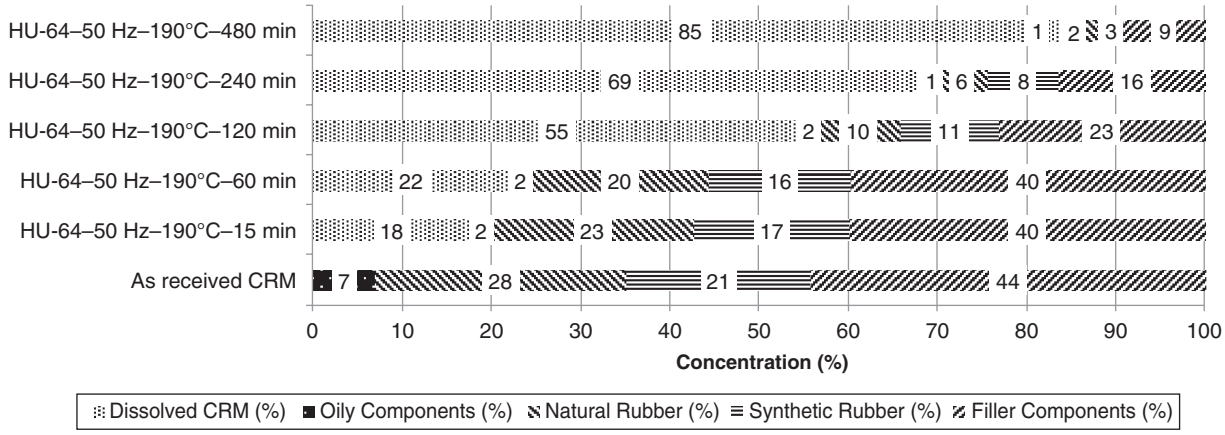


(d)

FIGURE 5 Component concentration in extracted CRM samples in comparison with original CRM: (*a*) HU-52–10 Hz–190°C, (*b*) HU-64–10 Hz–190°C, (*c*) HU-52–30 Hz–190°C, and (*d*) HU-64–30 Hz–190°C.



(a)



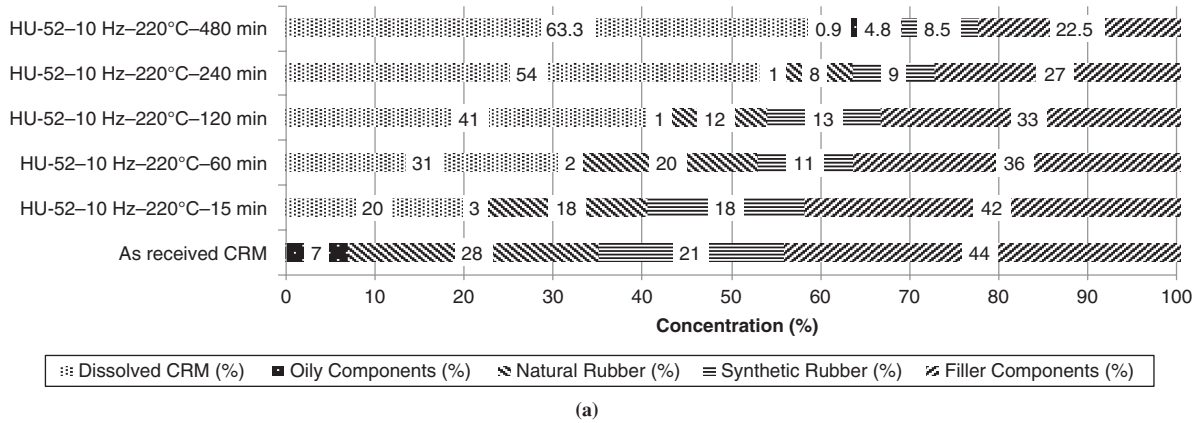
(b)

FIGURE 6 Component concentration in extracted CRM samples in comparison with original CRM: (*a*) HU-52–50 Hz–190°C and (*b*) HU-64–50 Hz–190°C.

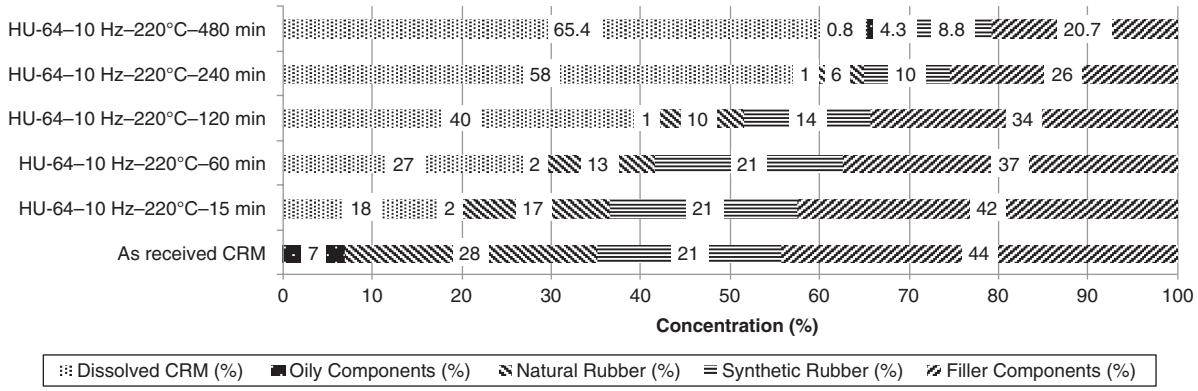
The same trend can be seen for the CRM extracted from the HU-64 CRMA samples interacted at 190°C and 50 Hz, which is illustrated in Figure 6*b.* After 480 min of interaction time, the CRM dissolution was 85%, with oily components reaching 1% and the natural rubber at about 2% from original values of 7% and 28%, respectively. The synthetic rubber decreased from 21% to 3% and the filler components decreased from 44% to 9%.

The extracted CRM compositional analysis was related to the rheological results of the same samples illustrated in Figure 3, *a* and *d.* The comparison shows that at a combination of high mixing speed (50 Hz) and moderate interaction temperature (190°C), the release of CRM is not only limited to the oily components and the natural rubber, but rather involves all CRM components, including the remaining synthetic rubber as well as the filler components. The release of CRM components coupled with the moderate interaction temperature (190°C) helps to initiate and sustain the formation of a 3-D entangled network structure that significantly enhances the CRMA rheological properties (G^* and δ). This can be explained by the occurrence of devulcanization effects that lead to the release of CRM components into the liquid phase of asphalt. However, at such moderate interaction conditions, the depolymerization effects for the released CRM polymeric components are not major; thus, the released CRM polymeric components are not readily destroyed (by depolymerization) and thus can undergo other processes involving the association within the CRMA liquid phase resulting in the produced 3-D entangled network structure. However, the mechanism of formation of the 3-D network structure in CRMA needs further investigation.

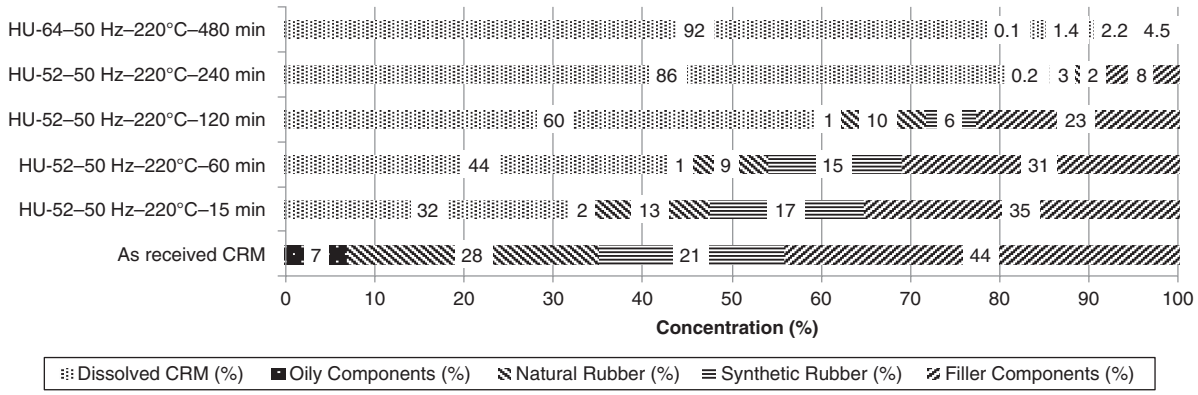
Figure 7 illustrates the change in compositional analysis of extracted CRM with an increase in interaction time for the following samples: HU-52–10 Hz–220°C (Figure 7*a*), HU-64–10 Hz–220°C (Figure 7*b*), HU-52–50 Hz–220°C (Figure 7*c*), and HU-64–50 Hz–220°C (Figure 7*d*). As shown in Figure 7*a,* for the CRM extracted from HU-52 CRMA, after 480 min of interaction time, CRM dissolution was 63.3% with the oily components being 0.9% and the natural rubber having a value of 4.8%. The synthetic rubber decreased to 8.5% and the filler components reached 22.5%. For the compositional analysis of CRM extracted from HU-64 asphalt, as illustrated in Figure 7*b,* after 480 min of interaction time, the total dissolution of extracted CRM was 65.4%, with oily components decreasing to 0.8%, natural rubber being 4.3%, synthetic rubber reaching 8.8%, and filler components of 20.7%. These results can be compared with the rheological properties of the same samples illustrated in Figure 3, *b* and *e.* From the comparison, it can be deduced that almost half the CRM particles dissolved in the CRMA liquid phase; however, as a result of the increased interaction temperature (220°C) and regardless of the reduced interaction speed (10 Hz), the excessive devulcanization and depolymerization effects were strong enough to annihilate the effect of the CRM-released components on the liquid phase of CRMA. A similar observation has been recorded in the literature (*8, 9*).



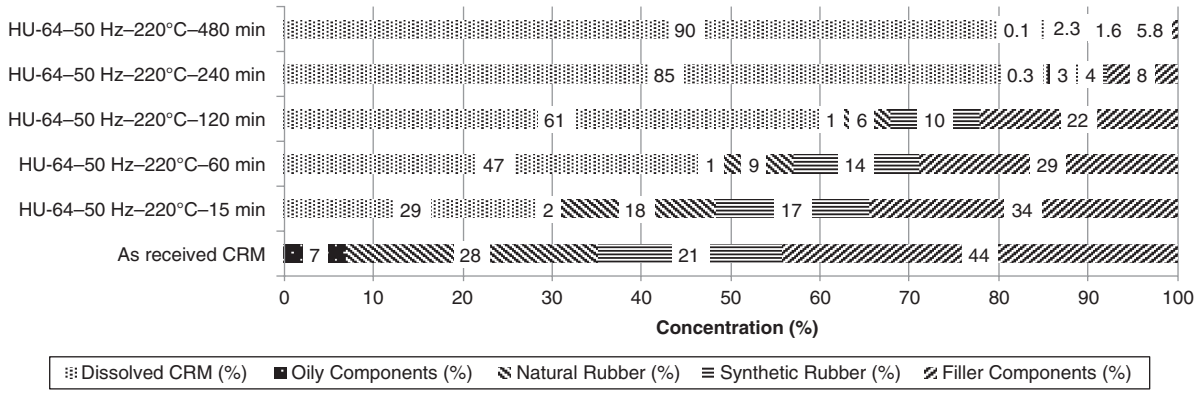
(a)



(b)



(c)



(d)

FIGURE 7 Component concentration in extracted CRM samples in comparison with original CRM: (*a*) HU-52–10 Hz–220°C, (*b*) HU-64–10 Hz–220°C, (*c*) HU-52–50 Hz–220°C, and (*d*) HU-64–50 Hz–220°C.

As shown in Figure 7*c,* for the extracted CRM from HU-52 CRMA interacted at 50 Hz and 220°C, extending the interaction time to 480 min resulted in a major release of CRM components, which manifested in CRM dissolution of 92% after 480 min of interaction time. The increase in dissolution of CRM is associated with a major release of most of the CRM components.

The same trend can be seen for the CRM extracted from the HU-64 CRMA samples interacted at 220°C and 50 Hz, as illustrated in Figure 7*d.* After 480 min of interaction time, the CRM dissolution was 90%, with oily components reaching 0.1% and the natural rubber about 2.3%. The synthetic rubber decreased to 1.6% and the filler components decreased to 5.8%. The amount of released CRM components is similar between the samples interacted at 190°C with 50 Hz at 480 min of interaction time and the samples interacted at 220°C with 50 Hz at 480 min of interaction time. However, comparison of the values of the rheological parameters, G^* and δ, expressed in Figure 3, *a* and *d,* and Figure 3, *c* and *f,* respectively, shows that with nearly similar CRM dissolved or released components, the effect of interaction temperature can dramatically enhance or deteriorate the properties of CRMA. As can be seen from Figure 3, *c* and *f,* the high interaction temperature (220°C) severely annihilated the modification effects of the released CRM components, even at almost 90% dissolution.

The case was different for interaction temperature of 190°C with interaction speed of 50 Hz. At lower CRM dissolution, the CRM release into the CRMA liquid phase had the effect of the formation of a 3-D entangled network structure that significantly enhanced the rheological properties of the CRMA.

FTIR Analysis

FTIR analysis was utilized to determine the state of existence of the released CRM components in the liquid phase of CRMA under the effect of the different interaction parameters utilized. Figure 8

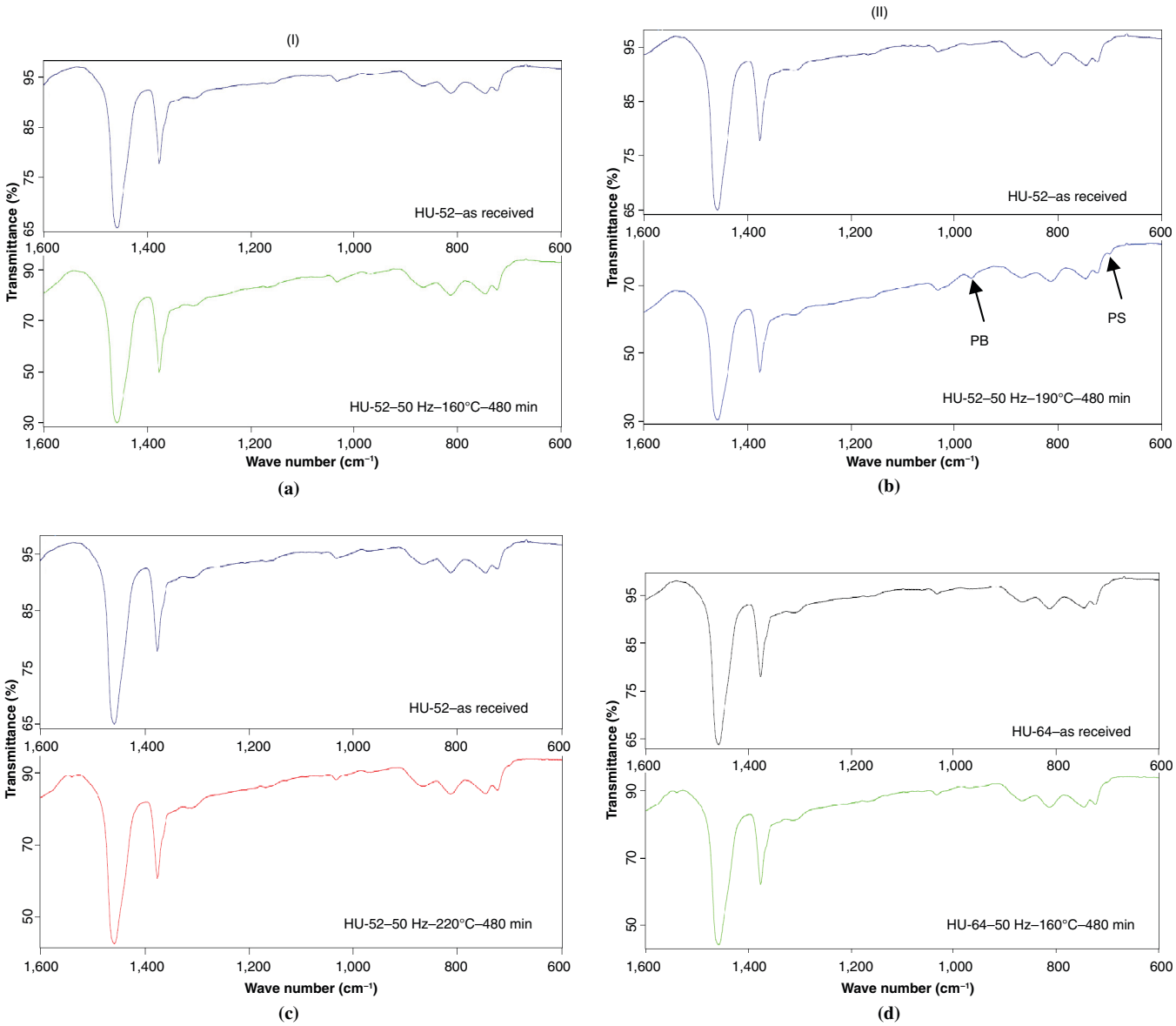


FIGURE 8 FTIR spectroscopes comparisons of received asphalts and samples interacted for 8 h: (*a*) HU-52 at 160°C and 50 Hz, (*b*) HU-52 at 190°C and 50 Hz, (*c*) HU-52 at 220°C and 50 Hz, and (*d*) HU-64 at 160°C and 50 Hz.

(continued on next page)

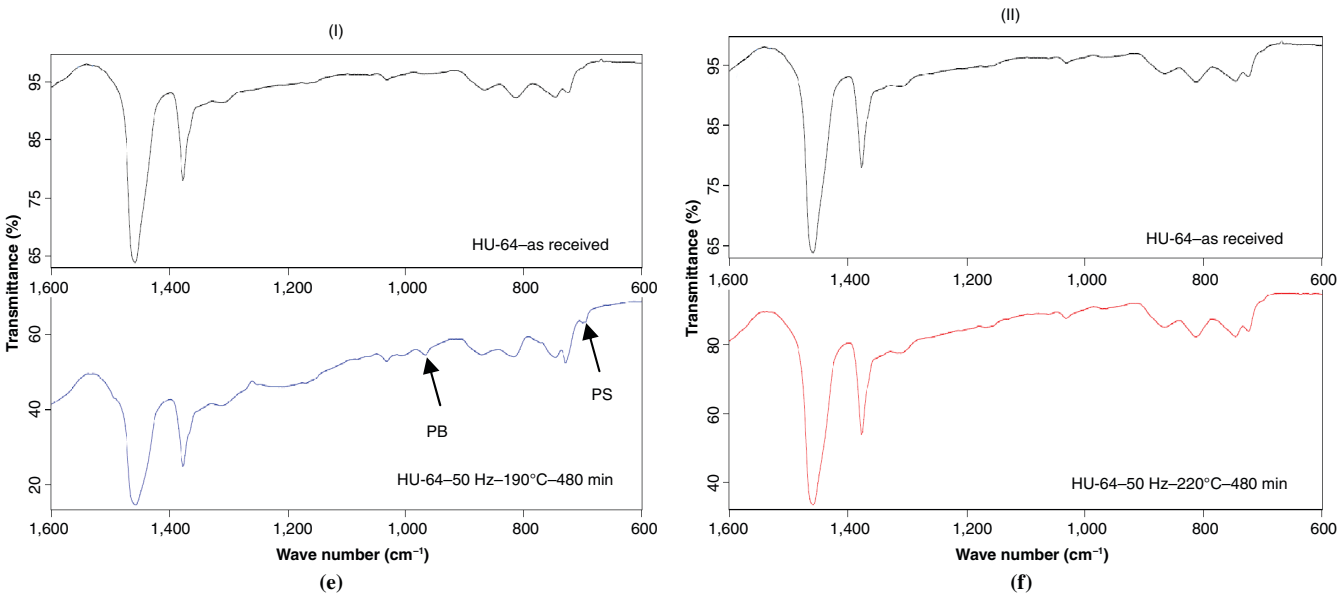


FIGURE 8 *(continued)* FTIR spectroscopes comparisons of received asphalts and samples interacted for 8 h: (*e*) HU-64 at 190°C and 50 Hz and (*f*) HU-64 at 220°C and 50 Hz (PB = polybutadiene; PS = polysterene). (Source: Bruker.)

illustrates the FTIR spectroscopic comparison of the received asphalts and samples interacted for 480 min at 160°C and 50 Hz, 190°C and 50 Hz, and 220°C and 50 Hz for HU-52 and HU-64.

As shown in Figure 8, *a* and *d,* even after 8 h of interaction time, peaks for the out-of-plane carbon–hydrogen bends of the aromatic ring that are supposed to be intense at 698 cm^{-1} for the polystyrene are not present. In addition, peaks at 966 cm^{-1} for the trans component in polybutadiene are not present. This result indicates that at lower interaction conditions (160°C and 50 Hz), the release of CRM components is minimal and the main CRM interaction with asphalt is the CRM absorbance of low molecular weight maltenes (*7*).

Figure 8, *b* and *e,* illustrates the existence of peaks for the out-of-plane carbon–hydrogen bends of the aromatic ring at 698 for the polystyrene (see the arrow for PS in Figure 8, *b* and *e*). In addition, peaks at 966 cm^{-1} for the trans component in polybutadiene can be seen (see the arrow for PB in Figure 8, *b* and *e*). These peaks indicate that at a combination of high interaction speed (50 Hz) and moderate interaction temperature (190°C), two mechanisms are involved in CRM interaction with asphalt. The first interaction is the CRM absorbance of low molecular weight maltenes. The second and most intense mechanism is the occurrence of devulcanization, leading to the partial dissolution of CRM in the liquid phase of asphalt.

As shown in Figure 8, *c* and *f,* the same observation of absence of distinctive peaks of either polystyrene and polybutadiene can be seen, indicating that at that combination of interaction conditions (220°C and 50 Hz), the devulcanization and depolymerization effects are dominating, leading to the annihilation of CRM-released components.

CONCLUSIONS

This study used rheological, TGA, and FTIR tests to investigate the nature of CRM components responsible for the formation of 3-D entangled network structure in CRMA. It was found that, depending on the dissolved amounts and released components of CRM and the CRMA interaction synthesis conditions involved, major enhancements in the CRMA rheological properties, in terms of its stiffness (G^*) and elasticity (δ), can be achieved through the development of 3-D entangled network structure in its liquid phase. The combination of moderate interaction temperature (190°C) and high interaction speed (50 Hz) was essential to control the CRM dissolution mechanism leading to the modification on the CRMA internal network structure that resulted in enhanced G^* and δ. Interacting the CRMA at 160° and 50 Hz resulted in CRMA with deteriorated physical properties as a result of limitation of CRM activities to swelling and minimal release. At 220°C interaction temperature, CRM depolymerization and devulcanization processes were severe, resulting in deterioration of the physical properties of the modified binder.

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